5.5 **GIBBS FUNCTION** ARTICLE

By definition the Gibbs Energy is

$$G = H - TS \qquad [1]$$

For an infinitesimal changes during a constant pressure process and substituting the definition of enthalpy, H=U+pV or $dH = dU + pdV + Vdp$

$$dG = dU + pdV - TdS \qquad [2]$$

And, for an infinitesimal change, we can use the definition of the specific heat capacity, i.e. $du = c_v dT$ [using lower case symbols for specific quantities] and assuming no change in the Gibbs Energy, i.e. the entropy change in the surroundings and system are equal

$$Tds = c_v dT + pdv \qquad [3]$$

And, for an ideal gas, $pv = RT$ so

$$ds = c_v \frac{dT}{T} + R\frac{dv}{v} \qquad [4]$$

In order to find the change in entropy between two states, 1 and 2, we can integrate this equation

$$\int_{s_1}^{s_2} ds = \int_{T_1}^{T_2} \frac{c_v}{T} dT + \int_{v_1}^{v_2} \frac{R}{v} dv \qquad [5]$$

Here we need to know that the integral of the fraction $(1/x)$ is $\ln x$. Hence, assuming c_p is approximately constant over the temperature range $(T_2 - T_1)$, then

$$(s_2 - s_1) = c_v \ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1} \qquad [6]$$

And for a process in which there is no entropy change, i.e. $s_2 = s_1$

$$c_v \ln\frac{T_2}{T_1} = -R\ln\frac{v_2}{v_1} \qquad [7]$$

or,

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\frac{R}{c_V}} \qquad [8]$$

given, $R = c_p - c_v$

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\frac{c_P - c_V}{c_V}} = \left(\frac{v_1}{v_2}\right)^{\gamma-1} \qquad [9]$$

where $\gamma = {}^{c_p}/_{c_v}$. We could have started from equation [1] and considered a constant volume process so that

$$dG = dh - vdp - T\Delta S \qquad [10]$$

then the alternative definition of specific heat capacity, i.e. $dh = c_p dT$ would, via the same steps, eventually lead to

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\gamma-1/\gamma} \qquad [11]$$

Expressions [9] and [11] can be combined to yield

$$\left(\frac{p_2}{p_1}\right) = \left(\frac{v_1}{v_2}\right)^{\gamma} \qquad [12]$$

Together expressions [9], [11] and [12] are known as the isentropic relations for an ideal gas and are useful when analysing a wide range of problems.

Gibbs energy is also sometimes known as the free energy or available energy. It describes the thermodynamic potential of a system; or its ability to do useful work. The concept is widely used in chemistry and bioenergetics. However, we can also use it in engineering to assess the available energy of system. For example, we know if we blow up a balloon and then let it go without tying off the end that it will fly around the room as the compressed air escapes from the balloon. The same concept, that is releasing compressed air, is being explored by some car manufacturers for its potential to power a car from a tank of compressed air.

Search for the Peugeot 208 Air Hybrid that was demonstrated at the 2014 Paris Auto Show, or for the MDI air-powered car (www.mdi.lu). Then watch the worked example in the next unit.